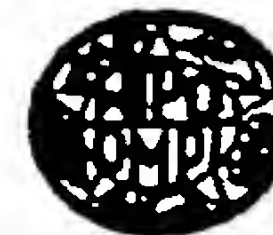


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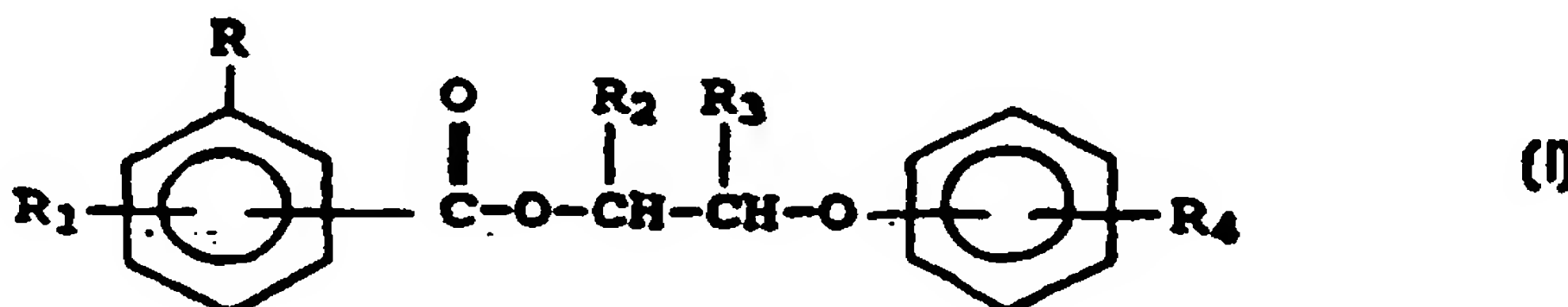
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(54) Title: AROMATIC ESTERS OF POLYALKYLPHENOXYALKANOLS AND FUEL COMPOSITIONS CONTAINING THE SAME

(57) Abstract

Aromatic esters of polyalkylphenoxyalkanols having formula (I), or a fuel soluble salt thereof, wherein R is hydroxy, nitro or $-(CH_2)_x-NR_5R_6$, wherein R_5 and R_6 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms and x is 0 or 1; R_1 is hydrogen, hydroxy, nitro or $-NR_7R_8$, wherein R_7 and R_8 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; R_2 and R_3 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and R_4 is a polyalkyl group having an average molecular weight in the range of about 450 to 5,000. The compounds of formula (I) are useful as fuel additives for the prevention and control of engine deposits.



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-1-

01 AROMATIC ESTERS OF POLYALKYLPHENOXYALKANOLS
02 AND FUEL COMPOSITIONS CONTAINING THE SAME

03
04 BACKGROUND OF THE INVENTION

05
06 Field of the Invention

07
08 This invention relates to aromatic esters of
09 polyalkylphenoxyalkanols and derivatives thereof. In a
10 further aspect, this invention relates to the use of these
11 compounds in fuel compositions to prevent and control engine
12 deposits.

13
14 Description of the Related Art

15
16 It is well known that automobile engines tend to form
17 deposits on the surface of engine components, such as
18 carburetor ports, throttle bodies, fuel injectors, intake
19 ports and intake valves, due to the oxidation and
20 polymerization of hydrocarbon fuel. These deposits, even
21 when present in relatively minor amounts, often cause
22 noticeable driveability problems, such as stalling and poor
23 acceleration. Moreover, engine deposits can significantly
24 increase an automobile's fuel consumption and production of
25 exhaust pollutants. Therefore, the development of effective
26 fuel detergents or "deposit control" additives to prevent or
27 control such deposits is of considerable importance and
28 numerous such materials are known in the art.

29
30 For example, aliphatic hydrocarbon-substituted phenols are
31 known to reduce engine deposits when used in fuel
32 compositions. U.S. Patent No. 3,849,085, issued
33 November 19, 1974 to Kreuz et al., discloses a motor fuel
34 composition comprising a mixture of hydrocarbons in the

01 gasoline boiling range containing about 0.01 to 0.25 volume
02 percent of a high molecular weight aliphatic
03 hydrocarbon-substituted phenol in which the aliphatic
04 hydrocarbon radical has an average molecular weight in the
05 range of about 500 to 3,500. This patent teaches that
06 gasoline compositions containing minor amounts of an
07 aliphatic hydrocarbon-substituted phenol not only prevent or
08 inhibit the formation of intake valve and port deposits in a
09 gasoline engine, but also enhance the performance of the
10 fuel composition in engines designed to operate at higher
11 operating temperatures with a minimum of decomposition and
12 deposit formation in the manifold of the engine.

13
14 Similarly, U.S. Patent No. 4,134,846, issued January 16,
15 1979 to Machleder et al., discloses a fuel additive
16 composition comprising a mixture of (1) the reaction product
17 of an aliphatic hydrocarbon-substituted phenol,
18 epichlorohydrin and a primary or secondary mono- or
19 polyamine, and (2) a polyalkylene phenol. This patent
20 teaches that such compositions show excellent carburetor,
21 induction system and combustion chamber detergency and, in
22 addition, provide effective rust inhibition when used in
23 hydrocarbon fuels at low concentrations.

24
25 Amino phenols are also known to function as
26 detergents/dispersants, antioxidants and anti-corrosion
27 agents when used in fuel compositions. U.S. Patent
28 No. 4,320,021, issued March 16, 1982 to R. M. Lange, for
29 example, discloses amino phenols having at least one
30 substantially saturated hydrocarbon-based substituent of at
31 least 30 carbon atoms. The amino phenols of this patent are
32 taught to impart useful and desirable properties to
33 oil-based lubricants and normally liquid fuels.

34

01 Similarly, U.S. Patent No. 3,149,933, issued September 22,
02 1964 to K. Ley et al., discloses hydrocarbon-substituted
03 amino phenols as stabilizers for liquid fuels.

04

05 U.S. Patent No. 4,386,939, issued June 7, 1983 to
06 R. M. Lange, discloses nitrogen-containing compositions
07 prepared by reacting an amino phenol with at least one 3- or
08 4-membered ring heterocyclic compound in which the hetero
09 atom is a single oxygen, sulfur or nitrogen atom, such as
10 ethylene oxide. The nitrogen-containing compositions of
11 this patent are taught to be useful as additives for
12 lubricants and fuels.

13

14 Nitro phenols have also been employed as fuel additives.
15 For example, U.S. Patent No. 4,347,148, issued August 31,
16 1982 to K. E. Davis, discloses nitro phenols containing at
17 least one aliphatic substituent having at least about 40
18 carbon atoms. The nitro phenols of this patent are taught
19 to be useful as detergents, dispersants, antioxidants and
20 demulsifiers for lubricating oil and fuel compositions.

21

22 Similarly, U.S. Patent No. 3,434,814, issued March 25, 1969
23 to M. Dubeck et al., discloses a liquid hydrocarbon fuel
24 composition containing a major quantity of a liquid
25 hydrocarbon of the gasoline boiling range and a minor amount
26 sufficient to reduce exhaust emissions and engine deposits
27 of an aromatic nitro compound having an alkyl, aryl,
28 aralkyl, alkanoyloxy, alkoxy, hydroxy or halogen
29 substituent.

30

31 More recently, certain poly(oxyalkylene) esters have been
32 shown to reduce engine deposits when used in fuel
33 compositions. U.S. Patent No. 5,211,721, issued May 18,
34 1993 to R. L. Sung et al., for example, discloses an oil

01 soluble polyether additive comprising the reaction product
02 of a polyether polyol with an acid represented by the
03 formula RCOOH in which R is a hydrocarbyl radical having
04 6 to 27 carbon atoms. The poly(oxyalkylene) ester compounds
05 of this patent are taught to be useful for inhibiting
06 carbonaceous deposit formation, motor fuel hazing, and as
07 ORI inhibitors when employed as soluble additives in motor
08 fuel compositions.

09
10 Poly(oxyalkylene) esters of amino- and nitrobenzoic acids
11 are also known in the art. For example, U.S. Patent
12 No. 2,714,607, issued August 2, 1955 to M. Matter, discloses
13 polyethoxy esters of aminobenzoic acids, nitrobenzoic acids
14 and other isocyclic acids. These polyethoxy esters are
15 taught to have excellent pharmacological properties and to
16 be useful as anesthetics, spasmolytics, analeptics and
17 bacteriostatics.

18
19 Similarly, U.S. Patent No. 5,090,914, issued February 25,
20 1992 to D. T. Reardan et al., discloses poly(oxyalkylene)
21 aromatic compounds having an amino or hydrazinocarbonyl
22 substituent on the aromatic moiety and an ester, amide,
23 carbamate, urea or ether linking group between the aromatic
24 moiety and the poly(oxyalkylene) moiety. These compounds
25 are taught to be useful for modifying macromolecular species
26 such as proteins and enzymes.

27
28 U.S. Patent No. 4,328,322, issued September 22, 1980 to
29 R. C. Baron, discloses amino- and nitrobenzoate esters of
30 oligomeric polyols, such as poly(ethylene) glycol. These
31 materials are used in the production of synthetic polymers
32 by reaction with a polyisocyanate.

33

34

01 U.S. Patent No. 4,859,210, issued August 22, 1989 to Franz
02 et al., discloses fuel compositions containing (1) one or
03 more polybutyl or polyisobutyl alcohols wherein the
04 polybutyl or polyisobutyl group has a number average
05 molecular weight of 324 to 3,000, or (2) a poly(alkoxylate)
06 of the polybutyl or polyisobutyl alcohol, or (3) a
07 carboxylate ester of the polybutyl or polyisobutyl alcohol.
08 This patent further teaches that when the fuel composition
09 contains an ester of a polybutyl or polyisobutyl alcohol,
10 the ester-forming acid group may be derived from saturated
11 or unsaturated, aliphatic or aromatic, acyclic or cyclic
12 mono- or polycarboxylic acids.

13

14 U.S. Patent Nos. 3,285,855, and 3,330,859 issued
15 November 15, 1966 and July 11, 1967 respectively, to Dexter
16 et al., disclose alkyl esters of dialkyl hydroxybenzoic and
17 hydroxyphenylalkanoic acids wherein the ester moiety
18 contains from 6 to 30 carbon atoms. These patents teach
19 that such esters are useful for stabilizing polypropylene
20 and other organic material normally subject to oxidative
21 deterioration. Similar alkyl esters containing hindered
22 dialkyl hydroxyphenyl groups are disclosed in U.S. Patent
23 No. 5,196,565, which issued March 23, 1993 to Ross.

24

25 U.S. Patent No. 5,196,142, issued March 23, 1993 to Mollet
26 et al., discloses alkyl esters of hydroxyphenyl carboxylic
27 acids wherein the ester moiety may contain up to 23 carbon
28 atoms. This patent teaches that such compounds are useful
29 as antioxidants for stabilizing emulsion-polymerized
30 polymers.

31

32 My prior U.S. Patent No. 5,407,452, issued April 18, 1995,
33 and corresponding International Application Publication No.
34 WO 95/04118, published February 9, 1995, disclose certain

01 poly(oxyalkylene) nitro and aminoaromatic esters having from
02 5 to 100 oxyalkylene units and teach the use of such
03 compounds as fuel additives for the prevention and control
04 of engine deposits.

05

06 Similarly, my prior U.S. Patent No. 5,427,591, issued
07 June 27, 1995, and corresponding International Application
08 Publication No. WO 94/14926, published July 7, 1994,
09 disclose certain poly(oxyalkylene) hydroxyaromatic esters
10 which are useful as fuel additives to control engine
11 deposits.

12

13 In addition, my prior U.S. Patent No. 5,380,345, issued
14 January 10, 1995, and corresponding International
15 Application Publication No. WO 95/15366, published June 8,
16 1995, disclose certain polyalkyl nitro and aminoaromatic
17 esters useful as deposit control additives for fuels.
18 Moreover, my prior International Application Publication No.
19 WO 95/11955, published May 4, 1995, discloses certain
20 polyalkyl hydroxyaromatic esters which are also useful as
21 deposit control fuel additives.

22

23

SUMMARY OF THE INVENTION

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25 I have now discovered certain aromatic esters of
26 polyalkylphenoxyalkanols which provide excellent control of
27 engine deposits, especially intake valve deposits, when
28 employed as fuel additives in fuel compositions.

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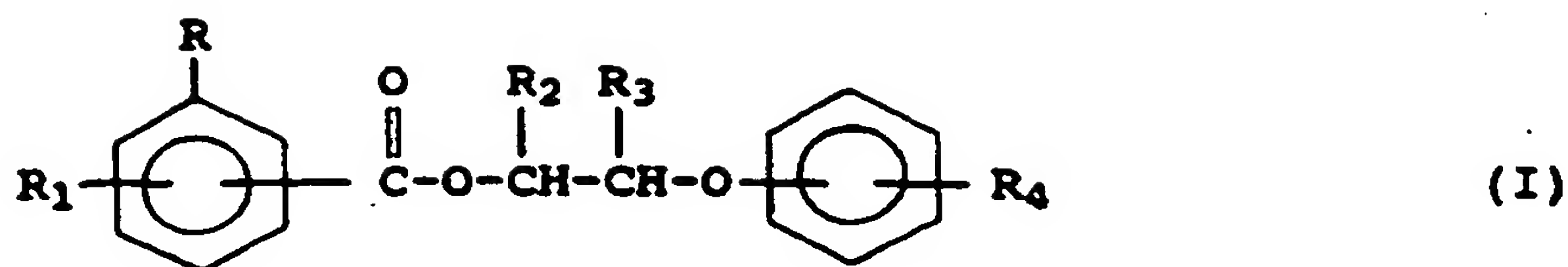
30 The compounds of the present invention include those having
31 the following formula and fuel soluble salts thereof:

32

33

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-7-



05 wherein R is hydroxy, nitro or $-(CH_2)_x-NR_5R_6$, wherein R_5 and
06 R_6 are independently hydrogen or lower alkyl having 1 to 6
07 carbon atoms and x is 0 or 1;

08
09 R_1 is hydrogen, hydroxy, nitro or $-NR_7R_8$, wherein R_7 and R_8
10 are independently hydrogen or lower alkyl having 1 to 6
11 carbon atoms;

12
13 R_2 and R_3 are independently hydrogen or lower alkyl having 1
14 to 6 carbon atoms; and

15
16 R_4 is a polyalkyl group having an average molecular weight
17 in the range of about 450 to 5,000.

18
19 The present invention further provides a fuel composition
20 comprising a major amount of hydrocarbons boiling in the
21 gasoline or diesel range and a deposit-controlling effective
22 amount of a compound of the present invention.

23
24 The present invention additionally provides a fuel
25 concentrate comprising an inert stable oleophilic organic
26 solvent boiling in the range of from about 150°F. to 400°F.
27 and from about 10 to 70 weight percent of a compound of the
28 present invention.

29
30 Among other factors, the present invention is based on the
31 surprising discovery that certain aromatic esters of
32 polyalkylphenoxyalkanols provide excellent control of engine
33 deposits, especially on intake valves, when employed as
34 additives in fuel compositions.

DETAILED DESCRIPTION OF THE INVENTION

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Based on performance (e.g. deposit control), handling properties and performance/cost effectiveness, the preferred compounds of the invention are those wherein R is nitro, amino, N-alkylamino, or $-\text{CH}_2\text{NH}_2$ (aminomethyl). More preferably, R is a nitro, amino or $-\text{CH}_2\text{NH}_2$ group. Most preferably, R is an amino or $-\text{CH}_2\text{NH}_2$ group, especially amino. Preferably, R_1 is hydrogen, hydroxy, nitro or amino. More preferably, R_1 is hydrogen or hydroxy. Most preferably, R_1 is hydrogen. Preferably, R_4 is a polyalkyl group having an average molecular weight in the range of about 500 to 3,000, more preferably about 700 to 3,000, and most preferably about 900 to 2,500. Preferably, the compound has a combination of preferred substituents.

Preferably, one of R_2 and R_3 is hydrogen or lower alkyl of 1 to 4 carbon atoms, and the other is hydrogen. More preferably, one of R_2 and R_3 is hydrogen, methyl or ethyl, and the other is hydrogen. Most preferably, R_2 is hydrogen, methyl or ethyl, and R_3 is hydrogen.

When R and/or R_1 is an N-alkylamino group, the alkyl group of the N-alkylamino moiety preferably contains 1 to 4 carbon atoms. More preferably, the N-alkylamino is N-methylamino or N-ethylamino.

Similarly, when R and/or R_1 is an N,N-dialkylamino group, each alkyl group of the N,N-dialkylamino moiety preferably contains 1 to 4 carbon atoms. More preferably, each alkyl group is either methyl or ethyl. For example, particularly preferred N,N-dialkylamino groups are N,N-dimethylamino, N-ethyl-N-methylamino and N,N-diethylamino groups.

01 A further preferred group of compounds are those wherein R
02 is amino, nitro, or $-\text{CH}_2\text{NH}_2$ and R_1 is hydrogen or hydroxy.
03 A particularly preferred group of compounds are those
04 wherein R is amino, R_1 , R_2 and R_3 are hydrogen, and R_4 is a
05 polyalkyl group derived from polyisobutene.

06
07 It is preferred that the R substituent is located at the
08 meta or, more preferably, the para position of the benzoic
09 acid moiety, i.e., para or meta relative to the carbonyloxy
10 group. When R_1 is a substituent other than hydrogen, it is
11 particularly preferred that this R_1 group be in a meta or
12 para position relative to the carbonyloxy group and in an
13 ortho position relative to the R substituent. Further, in
14 general, when R_1 is other than hydrogen, it is preferred
15 that one of R or R_1 is located para to the carbonyloxy group
16 and the other is located meta to the carbonyloxy group.
17 Similarly, it is preferred that the R_4 substituent on the
18 other phenyl ring is located para or meta, more preferably
19 para, relative to the ether linking group.

20
21 The compounds of the present invention will generally have a
22 sufficient molecular weight so as to be non-volatile at
23 normal engine intake valve operating temperatures
24 (about $200^\circ\text{--}250^\circ\text{C}$). Typically, the molecular weight of the
25 compounds of this invention will range from about 700 to
26 about 3,500, preferably from about 700 to about 2,500.

27
28 Fuel-soluble salts of the compounds of formula I can be
29 readily prepared for those compounds containing an amino or
30 substituted amino group and such salts are contemplated to
31 be useful for preventing or controlling engine deposits.
32 Suitable salts include, for example, those obtained by
33 protonating the amino moiety with a strong organic acid,
34

01 such as an alkyl- or arylsulfonic acid. Preferred salts are
02 derived from toluenesulfonic acid and methanesulfonic acid.

03

04 When the R or R₁ substituent is a hydroxy group, suitable
05 salts can be obtained by deprotonation of the hydroxy group
06 with a base. Such salts include salts of alkali metals,
07 alkaline earth metals, ammonium and substituted ammonium
08 salts. Preferred salts of hydroxy-substituted compounds
09 include alkali metal, alkaline earth metal and substituted
10 ammonium salts.

11

12 Definitions

13

14 As used herein, the following terms have the following
15 meanings unless expressly stated to the contrary.

16

17 The term "amino" refers to the group: -NH₂.

18

19 The term "N-alkylamino" refers to the group: -NHR_a wherein
20 R_a is an alkyl group. The term "N,N-dialkylamino" refers to
21 the group: -NR_bR_c, wherein R_b and R_c are alkyl groups.

22

23 The term "alkyl" refers to both straight- and branched-chain
24 alkyl groups.

25

26 The term "lower alkyl" refers to alkyl groups having 1 to
27 about 6 carbon atoms and includes primary, secondary and
28 tertiary alkyl groups. Typical lower alkyl groups include,
29 for example, methyl, ethyl, n-propyl, isopropyl, n-butyl,
30 sec-butyl, t-butyl, n-pentyl, n-hexyl and the like.

31

32 The term "polyalkyl" refers to an alkyl group which is
33 generally derived from polyolefins which are polymers or
34 copolymers of mono-olefins, particularly 1-mono-olefins,

01 such as ethylene, propylene, butylene, and the like.
02 Preferably, the mono-olefin employed will have 2 to about
03 24 carbon atoms, and more preferably, about 3 to 12 carbon
04 atoms. More preferred mono-olefins include propylene,
05 butylene, particularly isobutylene, 1-octene and 1-decene.
06 Polyolefins prepared from such mono-olefins include
07 polypropylene, polybutene, especially polyisobutene, and the
08 polyalphaolefins produced from 1-octene and 1-decene.

09
10 The term "fuel" or "hydrocarbon fuel" refers to normally
11 liquid hydrocarbons having boiling points in the range of
12 gasoline and diesel fuels.

13

14 General Synthetic Procedures

15

16 The polyalkylphenoxyalkyl aromatic esters of this invention
17 may be prepared by the following general methods and
18 procedures. It should be appreciated that where typical or
19 preferred process conditions (e.g., reaction temperatures,
20 times, mole ratios of reactants, solvents, pressures, etc.)
21 are given, other process conditions may also be used unless
22 otherwise stated. Optimum reaction conditions may vary with
23 the particular reactants or solvents used, but such
24 conditions can be determined by one skilled in the art by
25 routine optimization procedures.

26

27 Those skilled in the art will also recognize that it may be
28 necessary to block or protect certain functional groups
29 while conducting the following synthetic procedures. In
30 such cases, the protecting group will serve to protect the
31 functional group from undesired reactions or to block its
32 undesired reaction with other functional groups or with the
33 reagents used to carry out the desired chemical
34 transformations. The proper choice of a protecting group

-12-

01 for a particular functional group will be readily apparent
02 to one skilled in the art. Various protecting groups and
03 their introduction and removal are described, for example,
04 in T. W. Greene and P. G. M. Wuts, *Protective Groups in*
05 *Organic Synthesis*, Second Edition, Wiley, New York, 1991,
06 and references cited therein.

07
08 In the present synthetic procedures, a hydroxyl group will
09 preferably be protected, when necessary, as the benzyl or
10 tert-butyldimethylsilyl ether. Introduction and removal of
11 these protecting groups is well described in the art. Amino
12 groups may also require protection and this may be
13 accomplished by employing a standard amino protecting group,
14 such as a benzyloxycarbonyl or a trifluoroacetyl group.
15 Additionally, as will be discussed in further detail
16 hereinbelow, the aromatic esters of this invention having an
17 amino group on the aromatic moiety will generally be
18 prepared from the corresponding nitro derivative.
19 accordingly, in many of the following procedures, a nitro
20 group will serve as a protecting group for the amino moiety.

21
22 Moreover, the compounds of this invention having a $-CH_2NH_2$
23 group on the aromatic moiety will generally be prepared from
24 the corresponding cyano derivative, $-CN$. Thus, in many of
25 the following procedures, a cyano group will serve as a
26 protecting group for the $-CH_2NH_2$ moiety.

27
28 Synthesis

29
30 The polyalkylphenoxyalkyl aromatic esters of the present
31 invention may be prepared by a process which initially
32 involves hydroxyalkylation of a polyalkylphenol of the
33 formula:

34

01

02

03

04

05

06 wherein R_4 is as defined herein, with an alkylene carbonate
 07 of the formula:

08

09

10

11

12

13

14

15 wherein R_2 and R_3 are as defined herein, in the presence of
 16 a catalytic amount of an alkali metal hydride or hydroxide,
 17 or alkali metal salt, to provide a polyalkylphenoxyalkanol
 18 of the formula:

19

20

21

22

23

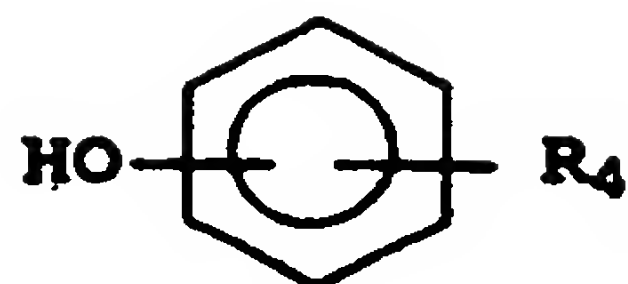
24 wherein R_2 , R_3 and R_4 are as defined herein.

25

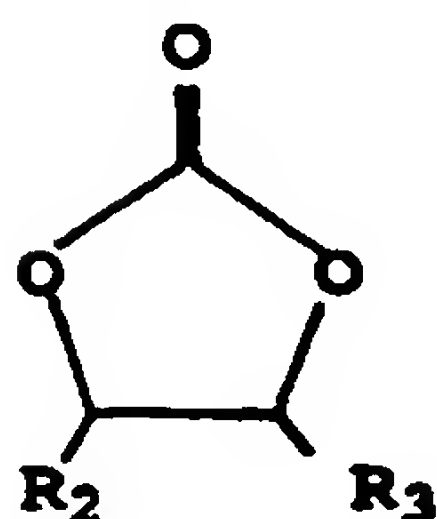
26 The polyalkylphenols of formula II are well known materials
 27 and are typically prepared by the alkylation of phenol with
 28 the desired polyolefin or chlorinated polyolefin. A further
 29 discussion of polyalkylphenols can be found, for example, in
 30 U.S. Patent No. 4,744,921 and U.S. Patent No. 5,300,701.

31

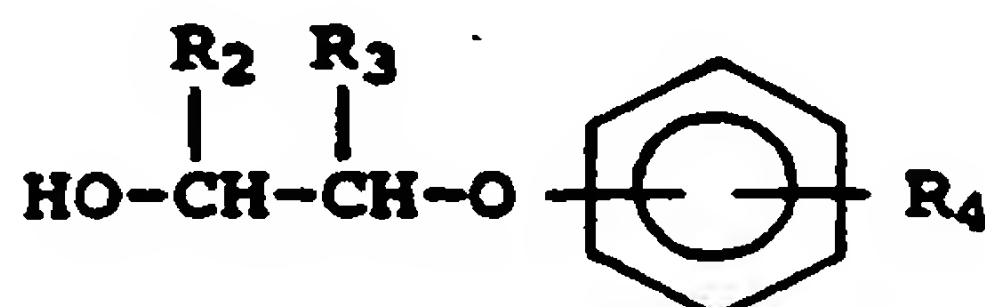
32 Accordingly, the polyalkylphenols of formula II may be
 33 prepared from the corresponding olefins by conventional
 34 procedures. For example, the polyalkylphenols of formula II



(II)



(III)



(IV)

01 above may be prepared by reacting the appropriate olefin or
02 olefin mixture with phenol in the presence of an alkylating
03 catalyst at a temperature of from about 25°C. to 150°C., and
04 preferably 30°C. to 100°C. either neat or in an essentially
05 inert solvent at atmospheric pressure. A preferred
06 alkylating catalyst is boron trifluoride. Molar ratios of
07 reactants may be used. Alternatively, molar excesses of
08 phenol can be employed, i.e., 2 to 3 equivalents of phenol
09 for each equivalent of olefin with unreacted phenol
10 recycled. The latter process maximizes monoalkylphenol.
11 Examples of inert solvents include heptane, benzene,
12 toluene, chlorobenzene and 250 thinner which is a mixture of
13 aromatics, paraffins and naphthenes.

14

15 The polyalkyl substituent on the polyalkylphenols employed
16 in the invention is generally derived from polyolefins which
17 are polymers or copolymers of mono-olefins, particularly
18 1-mono-olefins, such as ethylene, propylene, butylene, and
19 the like. Preferably, the mono-olefin employed will have 2
20 to about 24 carbon atoms, and more preferably, about 3 to 12
21 carbon atoms. More preferred mono-olefins include
22 propylene, butylene, particularly isobutylene, 1-octene and
23 1-decene. Polyolefins prepared from such mono-olefins
24 include polypropylene, polybutene, especially polyisobutene,
25 and the polyalphaolefins produced from 1-octene and
26 1-decene.

27

28 The preferred polyisobutenes used to prepare the presently
29 employed polyalkylphenols are polyisobutenes which comprise
30 at least about 20% of the more reactive methylvinylidene
31 isomer, preferably at least 50% and more preferably at least
32 70%. Suitable polyisobutenes include those prepared using
33 BF₃ catalysts. The preparation of such polyisobutenes in
34 which the methylvinylidene isomer comprises a high

-15-

01 percentage of the total composition is described in U.S.
02 Patent Nos. 4,152,499 and 4,605,808. Such polyisobutenes,
03 known as "reactive" polyisobutenes, yield high molecular
04 weight alcohols in which the hydroxyl group is at or near
05 the end of the hydrocarbon chain. Examples of suitable
06 polyisobutenes having a high alkylvinylidene content include
07 Ultravis 30, a polyisobutene having a number average
08 molecular weight of about 1300 and a methylvinylidene
09 content of about 74%, and Ultravis 10, a polyisobutene
10 having a number average molecular weight of about 950 and a
11 methylvinylidene content of about 76%, both available from
12 British Petroleum.

13
14 The alkylene carbonates of formula III are known compounds
15 which are available commercially or can be readily prepared
16 using conventional procedures. Suitable alkylene carbonates
17 include ethylene carbonate, propylene carbonate, 1,2-
18 butylene carbonate, 2,3-butylene carbonate, and the like. A
19 preferred alkylene carbonate is ethylene carbonate.

20
21 The catalyst employed in the reaction of the polyaklyphenol
22 and alkylene carbonate may be any of the well known
23 hydroxyalkylation catalysts. Typical hydroxyalkylation
24 catalysts include alkali metal hydrides, such as lithium
25 hydride, sodium hydride and potassium hydride, alkali metal
26 hydroxides, such as sodium hydroxide and potassium
27 hydroxide, and alkali metal salts, for example, alkali metal
28 halides, such as sodium chloride and potassium chloride, and
29 alkali metal carbonates, such as sodium carbonate and
30 potassium carbonate. The amount of catalyst employed will
31 generally range from about 0.01 to 1.0 equivalent,
32 preferably from about 0.05 to 0.3 equivalent.

33
34

01 The polyalkylphenol and alkylene carbonate are generally
02 reacted in essentially equivalent amounts in the presence of
03 the hydroxyalkylation catalyst at a temperature in the range
04 of about 100°C. to 210°C., and preferably from about 150°C.
05 to about 170°C. The reaction may take place in the presence
06 or absence of an inert solvent.

07
08 The time of reaction will vary depending on the particular
09 alkylphenol and alkylene carbonate reactants, the catalyst
10 used and the reaction temperature. Generally, the reaction
11 time will range from about two hours to about five hours.
12 The progress of the reaction is typically monitored by the
13 evolution of carbon dioxide. At the completion of the
14 reaction, the polyalkylphenoxyalkanol product is isolated
15 using conventional techniques.

16
17 The hydroxyalkylation reaction of phenols with alkylene
18 carbonates is well known in the art and is described, for
19 example, in U.S. Patent Nos. 2,987,555; 2,967,892; 3,283,030
20 and 4,341,905.

21
22 Alternatively, the polyalkylphenoxyalkanol product of
23 formula IV may be prepared by reacting the polyalkylphenol
24 of formula II with an alkylene oxide of the formula:



30 wherein R₂ and R₃ are as defined herein, in the presence of
31 a hydroxyalkylation catalyst as described above.

32
33 Suitable alkylene oxides of formula V include ethylene
34 oxide, propylene oxide, 1,2-butylene oxide, 2,3-butylene

01 oxide, and the like. A preferred alkylene oxide is ethylene
02 oxide.

03

04 In a manner similar to the reaction with alkylene carbonate,
05 the polyalkylphenol and alkylene oxide are reacted in
06 essentially equivalent or equimolar amounts in the presence
07 of 0.01 to 1.0 equivalent of a hydroxyalkylation catalyst,
08 such as sodium or potassium hydride, at a temperature in the
09 range of about 30°C. to about 150°C., for about 2 to about
10 24 hours. The reaction may be conducted in the presence or
11 absence of a substantially anhydrous inert solvent.

12 Suitable solvents include toluene, xylene, and the like.

13 Generally, the reaction conducted at a pressure sufficient
14 to contain the reactants and any solvent present, typically
15 at atmospheric or higher pressure. Upon completion of the
16 reaction, the polyalkylphenoxyalkanol is isolated by
17 conventional procedures.

18

19 The polyalkylphenoxyalkanol of formula IV is subsequently
20 reacted with a substituted benzoic acid of formula VI to
21 provide the aromatic ester compounds of formula I. This
22 reaction can be represented as follows:

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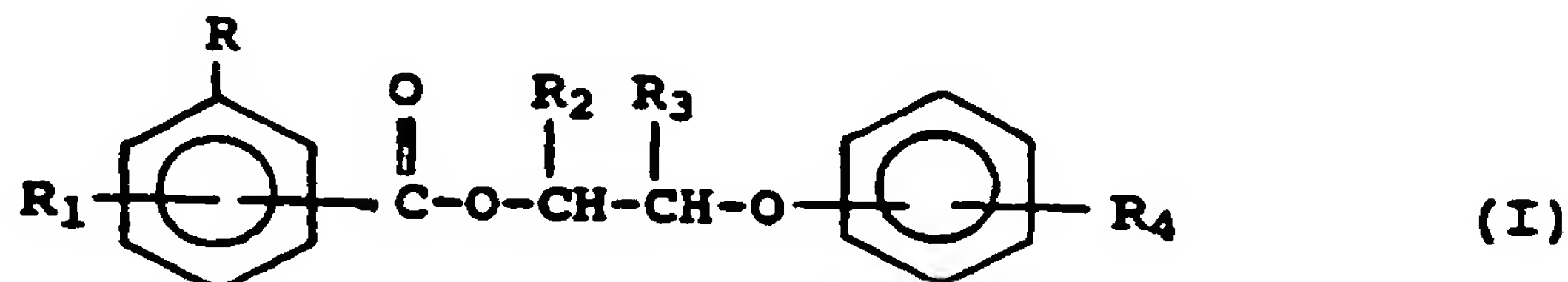
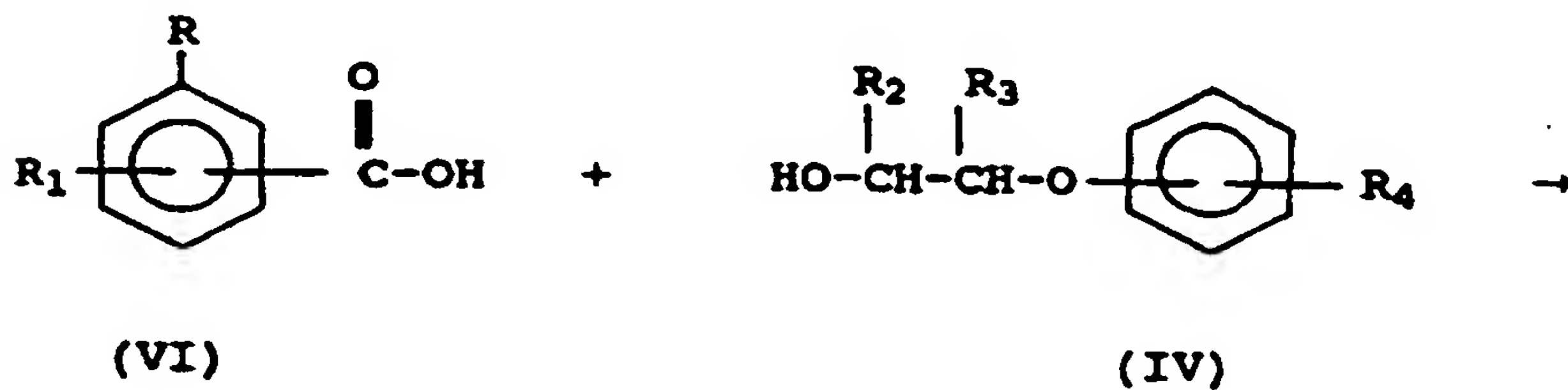
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32

33

34



01 wherein R, R₁, R₂, R₃ and R₄ are as defined herein, and
02 wherein any hydroxy or amino substituent on the substituted
03 benzoic acid of formula VI is preferably protected with a
04 suitable protecting group, for example, a benzyl or nitro
05 group, respectively. Moreover, a -CH₂NH₂ substituent on the
06 aromatic ring will preferably be protected by the use of a
07 cyano group, CN.

08
09 This reaction is typically conducted by contacting a
10 polyalkylphenoxyalkanol of formula IV with about 0.25 to
11 about 1.5 molar equivalents of the corresponding substituted
12 and protected benzoic acid of formula VI in the presence of
13 an acidic catalyst at a temperature in the range of about
14 70°C. to about 160°C. for about 0.5 to about 48 hours.
15 Suitable acid catalysts for this reaction include p-toluene
16 sulfonic acid, methanesulfonic acid and the like.
17 Optionally, the reaction can be conducted in the presence of
18 an inert solvent, such as benzene, toluene and the like.
19 The water generated by this reaction is preferably removed
20 during the course of the reaction, for example, by
21 azeotropic distillation.

22
23 The substituted benzoic acids of formula VI are generally
24 known compounds and can be prepared from known compounds
25 using conventional procedures or obvious modifications
26 thereof. Representative acids suitable for use as starting
27 materials include, for example, 2-aminobenzoic acid
28 (anthranilic acid), 3-aminobenzoic acid, 4-aminobenzoic
29 acid, 3-amino-4-hydroxybenzoic acid,
30 4-amino-3-hydroxybenzoic acid, 2-nitrobenzoic acid,
31 3-nitrobenzoic acid, 4-nitrobenzoic acid,
32 3-hydroxy-4-nitrobenzoic acid, 4-hydroxy-3-nitrobenzoic
33 acid. When the R substituent is -CH₂-NR₅R₆, suitable
34

01 starting materials include 4-cyanobenzoic acid and
 02 3-cyanobenzoic acid.

03

04 Preferred substituted benzoic acids include 3-nitrobenzoic
 05 acid, 4-nitrobenzoic acid, 3-hydroxy-4-nitrobenzoic acid,
 06 4-hydroxy-3-nitrobenzoic acid, 3-cyanobenzoic acid and
 07 4-cyanobenzoic acid.

08

09 The compounds formula I or their suitably protected analogs
 10 also can be prepared by reacting the polyalkylphenoxyalkanol
 11 of formula IV with an acid halide of the substituted benzoic
 12 acid of formula VI such as an acid chloride or acid bromide.
 13 This can be represented by the following reaction equation:

14

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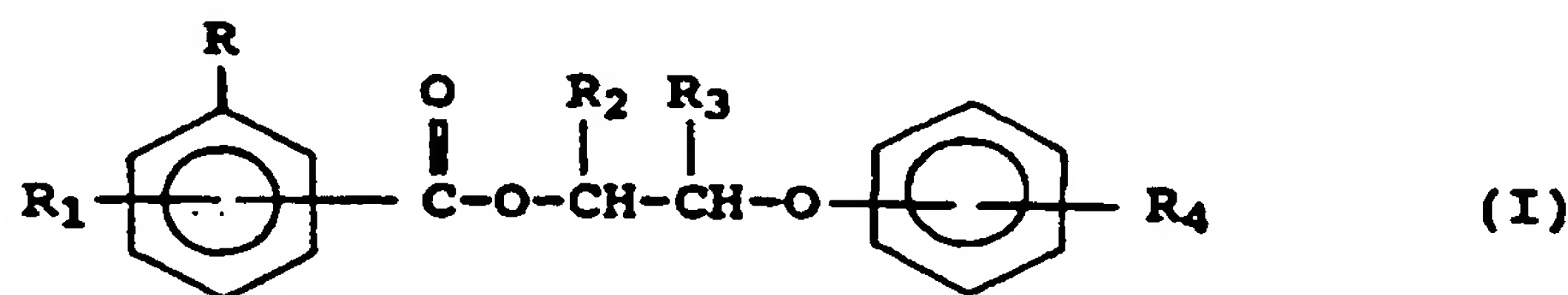
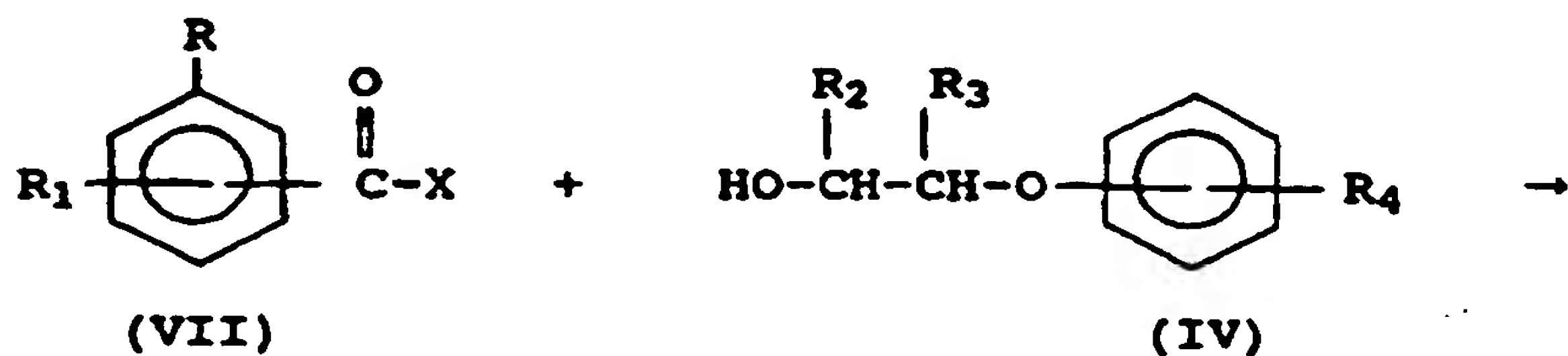
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25

26 wherein X is halide, typically chloride or bromide, and R,
 27 R₁, R₂, R₃ and R₄ are as defined herein above, and wherein
 28 any hydroxy or amino substituents on the acid halide of
 29 formula VII are preferably protected with a suitable
 30 protection group, for example, benzyl or nitro,
 31 respectively. Also, when R is —CH₂NR₅R₆, a suitable
 32 starting material is a cyanobenzoyl halide.

33

34



01 Typically, this reaction is conducted by contacting the
02 polyalkylphenoxyalkanol of formula IV with about 0.9 to
03 about 1.5 molar equivalents of the acid halide of
04 formula VII in an inert solvent, such as, for example,
05 toluene, dichloromethane, diethyl ether, and the like, at a
06 temperature in the range of about 25°C. to about 150°C. The
07 reaction is generally complete in about 0.5 to about
08 48 hours. Preferably, the reaction is conducted in the
09 presence of a sufficient amount of an amine capable of
10 neutralizing the acid generated during the reaction, such
11 as, for example, triethylamine, di(isopropyl)ethylamine,
12 pyridine or 4-dimethylaminopyridine.

13
14 When the benzoic acids of formula VI or acid halides of
15 formula VII contain a hydroxyl group, protection of the
16 aromatic hydroxyl groups may be accomplished using
17 well-known procedures. The choice of a suitable protecting
18 group for a particular hydroxybenzoic carboxylic acid will
19 be apparent to those skilled in the art. Various protecting
20 groups, and their introduction and removal, are described,
21 for example, in T. W. Greene and P. G. M. Wuts, *Protective*
22 *Groups in Organic Synthesis*, Second Edition, Wiley, New
23 York, 1991, and references cited therein.

24
25 After completion of the esterification, deprotection of the
26 aromatic hydroxyl group can also be accomplished using
27 conventional procedures. Appropriate conditions for this
28 deprotection step will depend upon the protecting group(s)
29 utilized in the synthesis and will be readily apparent to
30 those skilled in the art. For example, benzyl protecting
31 groups may be removed by hydrogenolysis under 1 to about 4
32 atmospheres of hydrogen in the presence of a catalyst, such
33 as palladium on carbon. Typically, this deprotection
34 reaction is conducted in an inert solvent, preferably a

-21-

01 mixture of ethyl acetate and acetic acid, at a temperature
02 of from about 0°C. to about 40°C. for about 1 to about
03 24 hours.
04

05 When the benzoic acids of formula VI or acyl halides of
06 formula VII have a free amino group (-NH₂) on the phenyl
07 moiety, it is generally desirable to first prepare the
08 corresponding nitro compound (i.e., where R and/or R₁ is a
09 nitro group) using the above-described synthetic procedures,
10 including preparation of the acyl halides, and then reduce
11 the nitro group to an amino group using conventional
12 procedures. Aromatic nitro groups may be reduced to amino
13 groups using a number of procedures that are well known in
14 the art. For example, aromatic nitro groups may be reduced
15 under catalytic hydrogenation conditions; or by using a
16 reducing metal, such as zinc, tin, iron and the like, in the
17 presence of an acid, such as dilute hydrochloric acid.
18 Generally, reduction of the nitro group by catalytic
19 hydrogenation is preferred. Typically, this reaction is
20 conducted using about 1 to 4 atmospheres of hydrogen and a
21 platinum or palladium catalyst, such as palladium on carbon.
22 The reaction is typically carried out at a temperature of
23 about 0°C. to about 100°C. for about 1 to 24 hours in an
24 inert solvent, such as ethanol, ethyl acetate and the like.
25 Hydrogenation of aromatic nitro groups is discussed in
26 further detail in, for example, P. N. Rylander, *Catalytic*
27 *Hydrogenation in Organic Synthesis*, pp. 113-137, Academic
28 Press (1979); and *Organic Synthesis, Collective Vol. I*,
29 Second Edition, pp. 240-241, John Wiley & Sons, Inc. (1941);
30 and references cited therein.
31

32 Likewise, when the benzoic acids of formula VI or acyl
33 halides of formula VII contain a -CH₂NH₂ group on the phenyl
34 moiety, it is generally desirable to first prepare the

01 corresponding cyano compounds (i.e., where R and/or R₁ is a
02 —CN group), and then reduce the cyano group to a —CH₂NH₂
03 group using conventional procedures. Aromatic cyano groups
04 may be reduced to —CH₂NH₂ groups using procedures well
05 known in the art. For example, aromatic cyano groups may be
06 reduced under catalytic hydrogenation conditions similar to
07 those described above for reduction of aromatic nitro groups
08 to amino groups. Thus, this reaction is typically conducted
09 using about 1 to 4 atmospheres of hydrogen and a platinum or
10 palladium catalyst, such as palladium on carbon. Another
11 suitable catalyst is a Lindlar catalyst, which is palladium
12 on calcium carbonate. The hydrogenation may be carried out
13 at temperatures of about 0°C. to about 100°C. for about 1 to
14 24 hours in an inert solvent such as ethanol, ethyl acetate,
15 and the like. Hydrogenation of aromatic cyano groups is
16 further discussed in the references cited above for
17 reduction of aromatic nitro groups.
18

19 The acyl halides of formula VII can be prepared by
20 contacting the corresponding benzoic acid compound of
21 formula VI with an inorganic acid halide, such as thionyl
22 chloride, phosphorous trichloride, phosphorous tribromide,
23 or phosphorous pentachloride; or with oxalyl chloride.
24 Typically, this reaction will be conducted using about 1 to
25 5 molar equivalents of the inorganic acid halide or oxalyl
26 chloride, either neat or in an inert solvent, such as
27 diethyl ether, at a temperature in the range of about 20°C.
28 to about 80°C. for about 1 to about 48 hours. A catalyst,
29 such as *N,N*-dimethylformamide, may also be used in this
30 reaction. Again it is preferred to first protect any
31 hydroxy or amino substituents before converting the benzoic
32 acid to the acyl halide.
33
34

Fuel Compositions

01

02

03 The compounds of the present invention are useful as
04 additives in hydrocarbon fuels to prevent and control engine
05 deposits, particularly intake valve deposits. The proper
06 concentration of additive necessary to achieve the desired
07 deposit control varies depending upon the type of fuel
08 employed, the type of engine, and the presence of other fuel
09 additives.

10

11 In general, the concentration of the compounds of this
12 invention in hydrocarbon fuel will range from about 50 to
13 about 2500 parts per million (ppm) by weight, preferably
14 from 75 to 1,000 ppm. When other deposit control additives
15 are present, a lesser amount of the present additive may be
16 used.

17

18 The compounds of the present invention may be formulated as
19 a concentrate using an inert stable oleophilic (i.e.,
20 dissolves in gasoline) organic solvent boiling in the range
21 of about 150°F. to 400°F. (about 65°C. to 205°C.).
22 Preferably, an aliphatic or an aromatic hydrocarbon solvent
23 is used, such as benzene, toluene, xylene or higher-boiling
24 aromatics or aromatic thinners. Aliphatic alcohols
25 containing about 3 to 8 carbon atoms, such as isopropanol,
26 isobutylcarbinol, n-butanol and the like, in combination
27 with hydrocarbon solvents are also suitable for use with the
28 present additives. In the concentrate, the amount of the
29 additive will generally range from about 10 to about
30 70 weight percent, preferably 10 to 50 weight percent, more
31 preferably from 20 to 40 weight percent.

32 In gasoline fuels, other fuel additives may be employed with
33 the additives of the present invention, including, for
34 example, oxygenates, such as t-butyl methyl ether, antiknock

01 agents, such as methylcyclopentadienyl manganese
02 tricarbonyl, and other dispersants/detergents, such as
03 hydrocarbyl amines, hydrocarbyl poly(oxyalkylene) amines,
04 hydrocarbyl poly(oxyalkylene) aminocarbamates, or
05 succinimides. Additionally, antioxidants, metal
06 deactivators and demulsifiers may be present.

07

08 In diesel fuels, other well-known additives can be employed,
09 such as pour point depressants, flow improvers, cetane
10 improvers, and the like.

11

12 A fuel-soluble, nonvolatile carrier fluid or oil may also be
13 used with the aromatic esters of this invention. The
14 carrier fluid is a chemically inert hydrocarbon-soluble
15 liquid vehicle which substantially increases the nonvolatile
16 residue (NVR), or solvent-free liquid fraction of the fuel
17 additive composition while not overwhelmingly contributing
18 to octane requirement increase. The carrier fluid may be a
19 natural or synthetic oil, such as mineral oil, refined
20 petroleum oils, synthetic polyalkanes and alkenes, including
21 hydrogenated and unhydrogenated polyalphaolefins, and
22 synthetic polyoxyalkylene-derived oils, such as those
23 described, for example, in U.S. Patent No. 4,191,537 to
24 Lewis, and polyesters, such as those described, for example,
25 in U.S. Patent Nos. 3,756,793 to Robinson and 5,004,478 to
26 Vogel et al., and in European Patent Application
27 Nos. 356,726, published March 7, 1990, and 382,159,
28 published August 16, 1990.

29

30 These carrier fluids are believed to act as a carrier for
31 the fuel additives of the present invention and to assist in
32 removing and retarding deposits. The carrier fluid may also
33 exhibit synergistic deposit control properties when used in

34

01 combination with a polyalkyl aromatic ester of this
02 invention.

03

04 The carrier fluids are typically employed in amounts ranging
05 from about 100 to about 5000 ppm by weight of the
06 hydrocarbon fuel, preferably from 400 to 3000 ppm of the
07 fuel. Preferably, the ratio of carrier fluid to deposit
08 control additive will range from about 0.5:1 to about 10:1,
09 more preferably from 1:1 to 4:1, most preferably about 2:1.

10

11 When employed in a fuel concentrate, carrier fluids will
12 generally be present in amounts ranging from about 20 to
13 about 60 weight percent, preferably from 30 to 50 weight
14 percent.

15

16

PREPARATIONS AND EXAMPLES

17

18 A further understanding of the invention can be had in the
19 following nonlimiting Examples. Wherein unless expressly
20 stated to the contrary, all temperatures and temperature
21 ranges refer to the Centigrade system and the term "ambient"
22 or "room temperature" refers to about 20°C.-25°C. The term
23 "percent" or "%" refers to weight percent and the term
24 "mole" or "moles" refers to gram moles. The term
25 "equivalent" refers to a quantity of reagent equal in moles,
26 to the moles of the preceding or succeeding reactant recited
27 in that example in terms of finite moles or finite weight or
28 volume. Where given, proton-magnetic resonance spectrum
29 (p.m.r. or n.m.r.) were determined at 300 MHz, signals are
30 assigned as singlets (s), broad singlets (bs), doublets (d),
31 double doublets (dd), triplets (t), double triplets (dt),
32 quartets (q), and multiplets (m), and cps refers to cycles
33 per second.

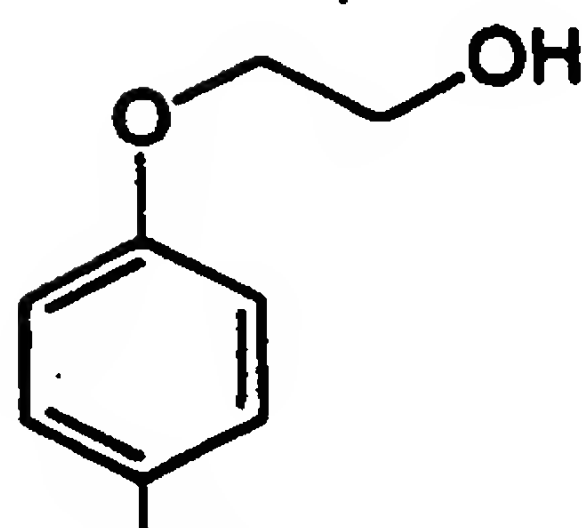
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-26-

Example 1Preparation of Polyisobutyl Phenol

To a flask equipped with a magnetic stirrer, reflux condenser, thermometer, addition funnel and nitrogen inlet was added 203.2 grams of phenol. The phenol was warmed to 40°C. and the heat source was removed. Then, 73.5 milliliters of boron trifluoride etherate was added dropwise. 1040 grams of Ultravis 10 Polyisobutene (molecular weight 950, 76% methylvinylidene, available from British Petroleum) was dissolved in 1,863 milliliters of hexane. The polyisobutene was added to the reaction at a rate to maintain the temperature between 22°C-27°C. The reaction mixture was stirred for 16 hours at room temperature. Then, 400 milliliters of concentrated ammonium hydroxide was added, followed by 2,000 milliliters of hexane. The reaction mixture was washed with water (3 x 2,000 milliliters), dried over magnesium sulfate, filtered and the solvents removed under vacuum to yield 1,056.5 grams of a crude reaction product. The crude reaction product was determined to contain 80% of the desired product by proton NMR and chromatography on silica gel eluting with hexane, followed by hexane: ethylacetate: ethanol (93:5:2).

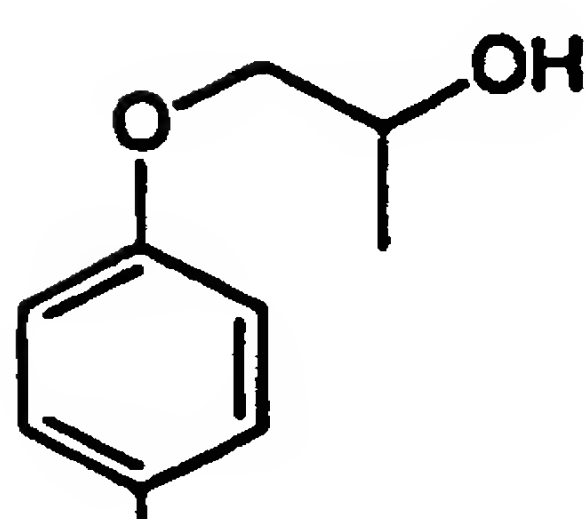
-27-

Example 2Preparation of

PB (molecular weight ~ 950)

1.1 grams of a 35 weight percent dispersion of potassium hydride in mineral oil and 4- polyisobutyl phenol (99.7 grams, prepared as in Example 1) were added to a flask equipped with a magnetic stirrer, reflux condensor, nitrogen inlet and thermometer. The reaction was heated at 130°C for one hour and then cooled to 100°C. Ethylene carbonate (8.6 grams) was added and the mixture was heated at 160°C for 16 hours. The reaction was cooled to room temperature and one milliliter of isopropanol was added. The reaction was diluted with one liter of hexane, washed three times with water and once with brine. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvents removed in vacuo to yield 98.0 grams of the desired product as a yellow oil.

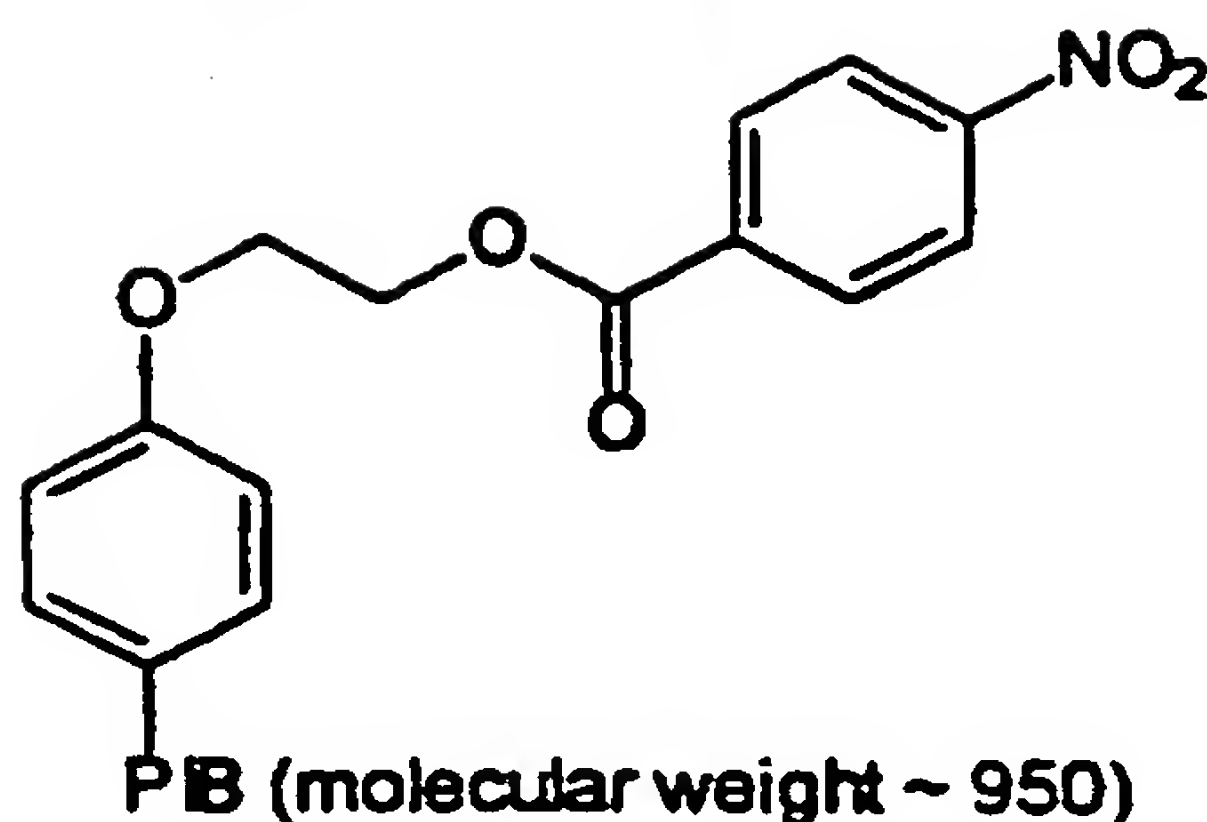
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Example 3Preparation of

PIB (molecular weight ~ 950)

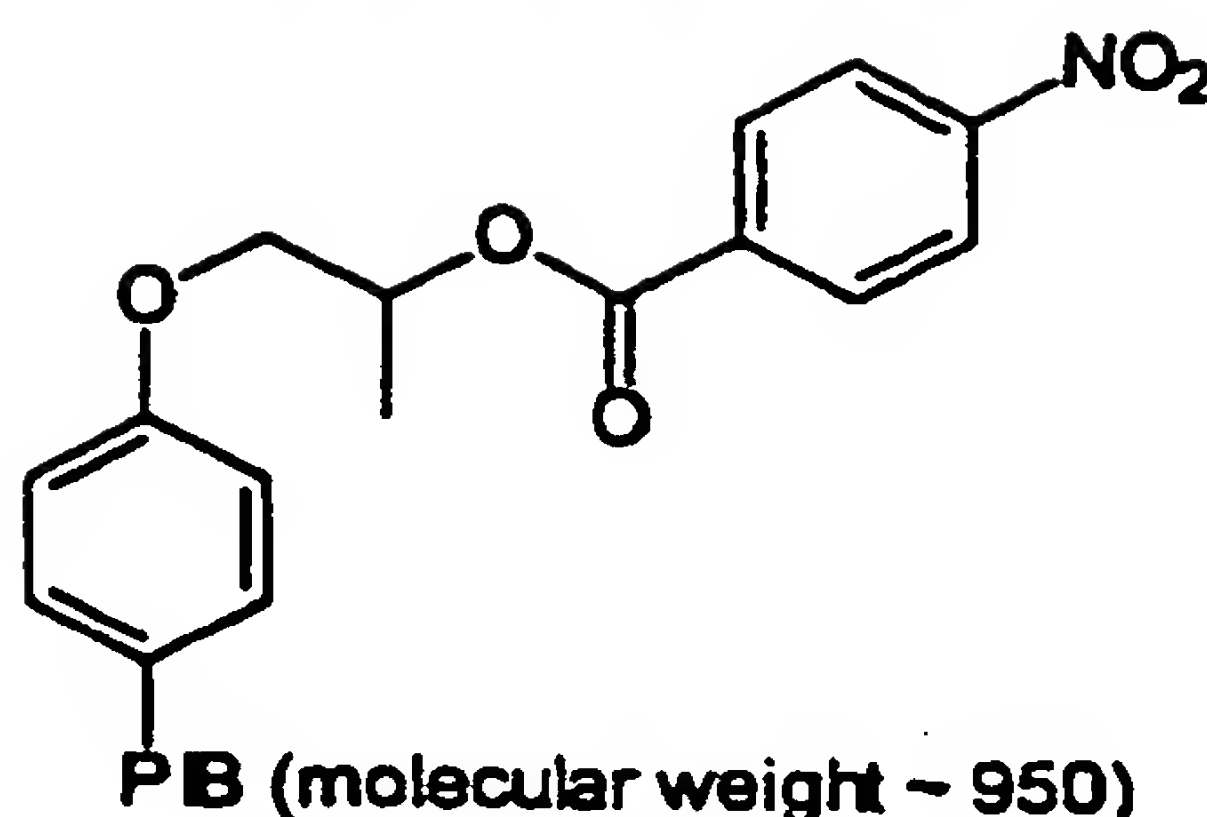
15.1 grams of a 35 weight percent dispersion of potassium hydride in mineral oil and 4- polyisobutyl phenol (1378.5 grams, prepared as in Example 1) were added to a flask equipped with a mechanical stirrer, reflux condensor, nitrogen inlet and thermometer. The reaction was heated at 130°C for one hour and then cooled to 100°C. Propylene carbonate (115.7 milliliters) was added and the mixture was heated at 160°C for 16 hours. The reaction was cooled to room temperature and ten milliliters of isopropanol were added. The reaction was diluted with ten liters of hexane, washed three times with water and once with brine. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvents removed in vacuo to yield 1301.7 grams of the desired product as a yellow oil.

-29-

Example 4Preparation of

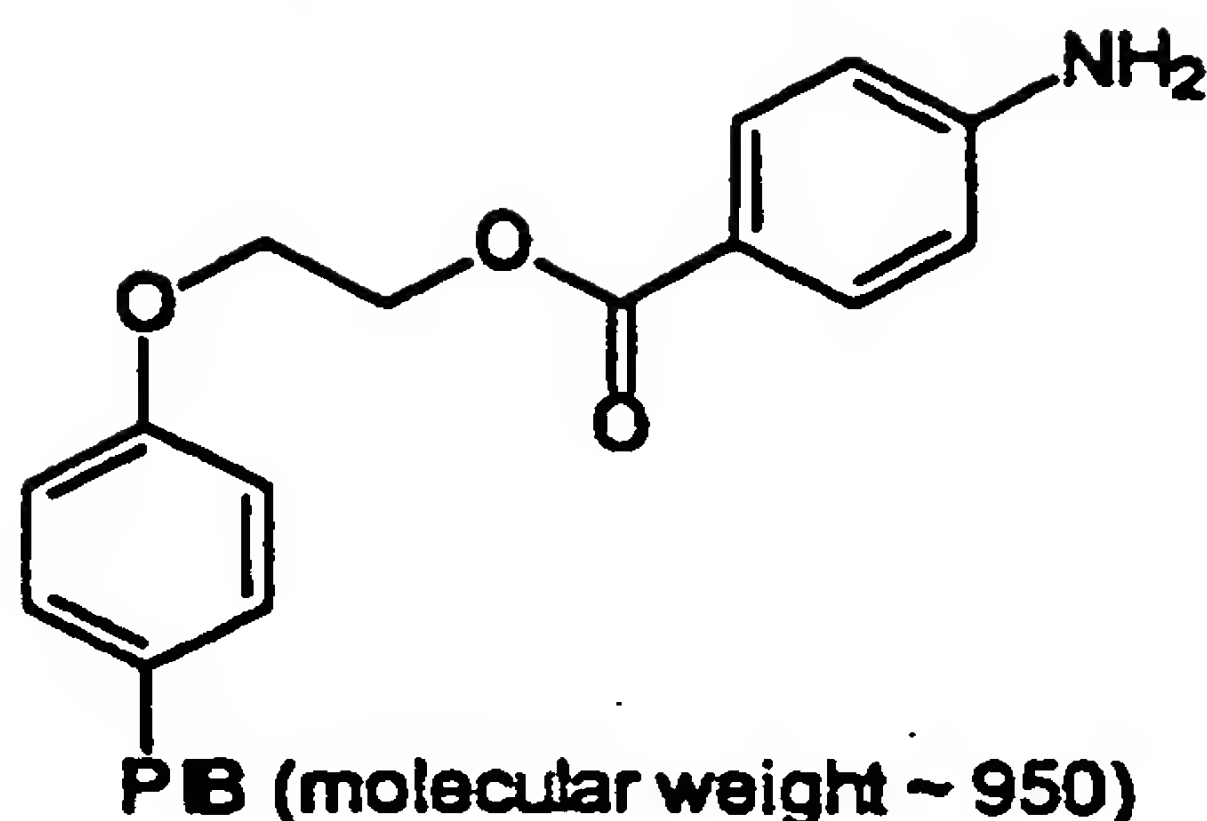
To a flask equipped with a magnetic stirrer, thermometer, Dean-Stark trap, reflux condensor and nitrogen inlet was added 15.0 grams of the alcohol from Example 2, 2.6 grams of 4-nitrobenzoic acid and 0.24 grams of *p*-toluenesulfonic acid. The mixture was stirred at 130°C for sixteen hours, cooled to room temperature and diluted with 200 mL of hexane. The organic phase was washed twice with saturated aqueous sodium bicarbonate followed by once with saturated aqueous sodium chloride. The organic layer was then dried over anhydrous magnesium sulfate, filtered and the solvents removed in vacuo to yield 15.0 grams of the desired product as a brown oil. The oil was chromatographed on silica gel, eluting with hexane/ethyl acetate (9:1) to afford 14.0 grams of the desired ester as a yellow oil. ¹H NMR (CDCl₃) δ 8.3 (AB quartet, 4H), 7.25 (d, 2H), 6.85 (d, 2H), 4.7 (t, 2H), 4.3 (t, 2H), 0.7-1.6 (m, 137H).

-30-

Example 5Preparation of

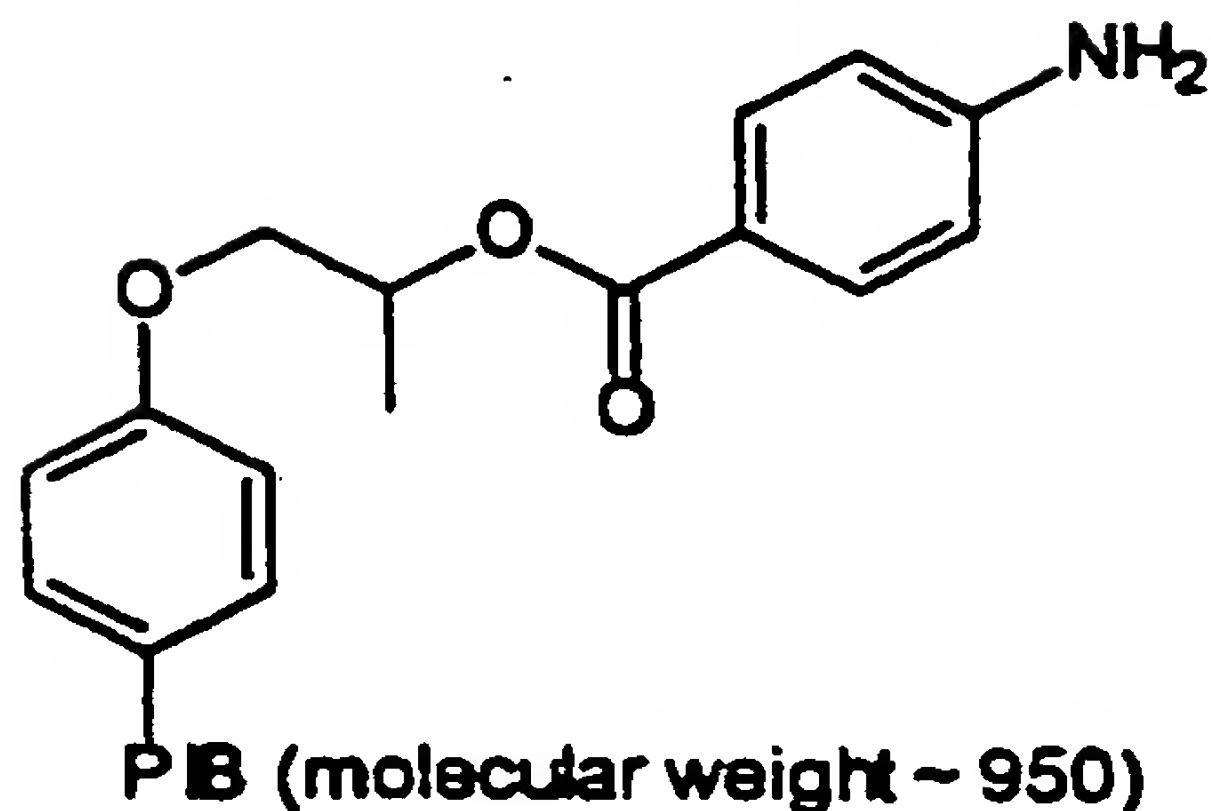
To a flask equipped with a magnetic stirrer, thermometer, Dean-Stark trap, reflux condensor and nitrogen inlet was added 15.0 grams of the alcohol from Example 3, 2.7 grams of 4-nitrobenzoic acid and 0.23 grams of *p*-toluenesulfonic acid. The mixture was stirred at 130°C for sixteen hours, cooled to room temperature and diluted with 200 mL of hexane. The organic phase was washed twice with saturated aqueous sodium bicarbonate followed by once with saturated aqueous sodium chloride. The organic layer was then dried over anhydrous magnesium sulfate, filtered and the solvents removed in vacuo to yield 16.0 grams of the desired product as a brown oil. The oil was chromatographed on silica gel, eluting with hexane/ethyl acetate (8:2) to afford 15.2 grams of the desired ester as a brown oil. ¹H NMR (CDCl₃) δ 8.2 (AB quartet, 4H), 7.25 (d, 2H), 6.85 (d, 2H), 5.55 (hx, 1H), 4.1 (t, 2H), 0.6-1.8 (m, 140H).

-31-

Example 6Preparation of

A solution of 9.4 grams of the product from Example 4 in 100 milliliters of ethyl acetate containing 1.0 gram of 10% palladium on charcoal was hydrogenolyzed at 35-40 psi for 16 hours on a Parr low-pressure hydrogenator. Catalyst filtration and removal of the solvent in vacuo yield 7.7 grams of the desired product as a yellow oil. ^1H NMR (CDCl_3) δ 7.85 (d, 2H), 7.3 (d, 2H), 6.85 (d, 2H), 6.6 (d, 2H), 4.6 (t, 2H), 4.25 (t, 2H), 4.05 (bs, 2H), 0.7-1.6 (m, 137H).

-32-

Example 7Preparation of

A solution of 15.2 grams of the product from Example 5 in 200 milliliters of ethyl acetate containing 1.0 gram of 10% palladium on charcoal was hydrogenolyzed at 35-40 psi for 16 hours on a Parr low-pressure hydrogenator. Catalyst filtration and removal of the solvent in vacuo yield 15.0 grams of the desired product as a brown oil. ^1H NMR ($\text{CDCl}_3/\text{D}_2\text{O}$) δ 7.85 (d, 2H), 7.25 (d, 2H), 6.85 (d, 2H), 6.6 (d, 2H), 5.4 (hx, 1H), 3.8-4.2 (m, 4H), 0.6-1.8 (m, 140H).

Example 8Single-Cylinder Engine Test

The test compounds were blended in gasoline and their deposit reducing capacity determined in an ASTM/CFR single-cylinder engine test.

A Waukesha CFR single-cylinder engine was used. Each run was carried out for 15 hours, at the end of which time the intake valve was removed, washed with hexane and weighed. The previously determined weight of the clean valve was

-33-

01 subtracted from the weight of the value at the end of the
02 run. The differences between the two weights is the weight
03 of the deposit. A lesser amount of deposit indicates a
04 superior additive. The operating conditions of the test
05 were as follows: water jacket temperature 200°F; vacuum of
06 12 in Hg, air-fuel ratio of 12, ignition spark timing of
07 400 BTC; engine speed is 1800 rpm; the crankcase oil is a
08 commercial 30W oil.

09

10 The amount of carbonaceous deposit in milligrams on the
11 intake valves is reported for each of the test compounds in
12 Table I.

13

TABLE I

14

Intake Valve Deposit Weight
(in milligrams)

15

16

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19

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¹At 150 parts per million actives (ppma).

The base fuel employed in the above single-cylinder engine tests was a regular octane unleaded gasoline containing no fuel detergent. The test compounds were admixed with the base fuel to give a concentration of 150 ppma (parts per million actives).

The data in Table I illustrates the significant reduction in intake valve deposits provided by the aromatic esters of polyalkylphenoxyalkanols of the present invention (Examples 4 and 6) compared to the base fuel.

01 WHAT IS CLAIMED IS:

02

03 1. A compound of the formula:

04

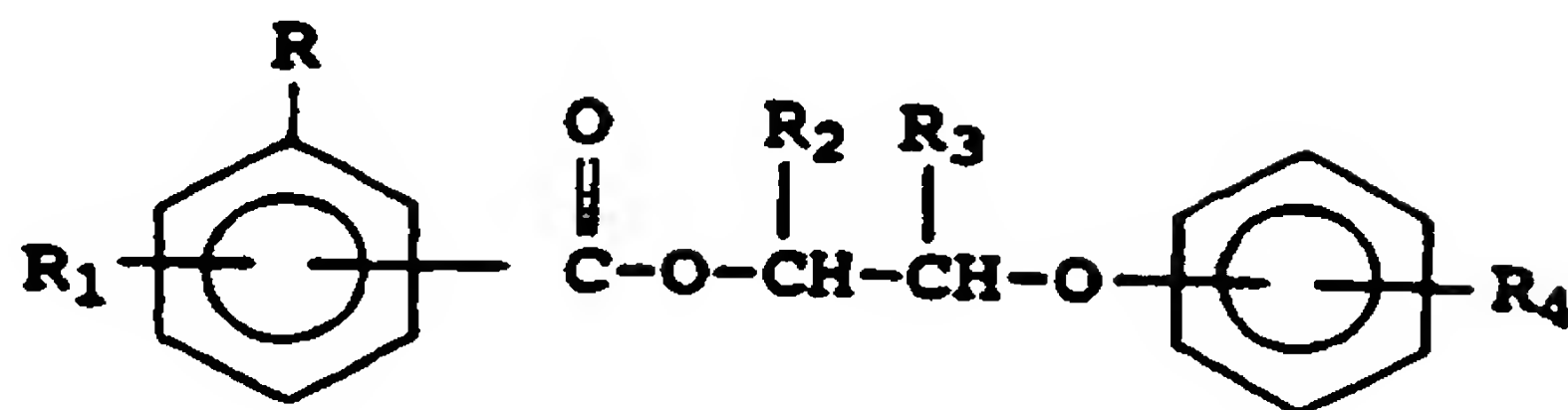
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or a fuel soluble salt thereof, wherein R is hydroxy, nitro or $-(CH_2)_x-NR_5R_6$, wherein R_5 and R_6 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms and x is 0 or 1;

R_1 is hydrogen, hydroxy, nitro or $-NR_7R_8$, wherein R_7 and R_8 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms;

R_2 and R_3 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and

R_4 is a polyalkyl group having an average molecular weight in the range of about 450 to 5,000.

2. The compound according to Claim 1, wherein R is nitro, amino or $-CH_2NH_2$.

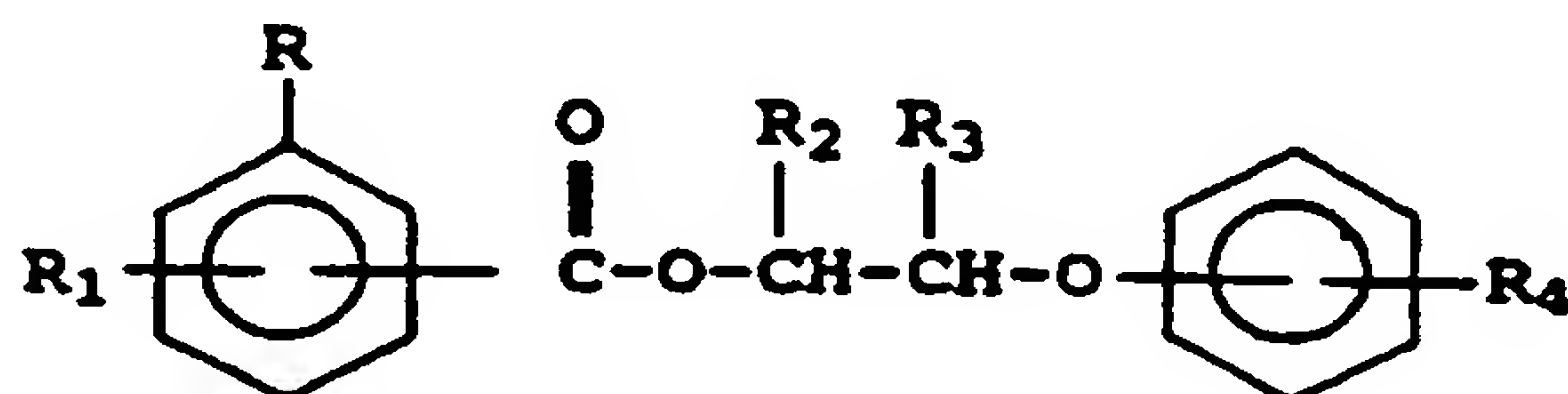
3. The compound according to Claim 2, wherein R is amino, or $-CH_2NH_2$.

4. The compound according to Claim 3, wherein R is amino.

5. The compound according to Claim 1, wherein R_1 is hydrogen, hydroxy, nitro or amino.

- 01 6. The compound according to Claim 5, wherein R_1 is
02 hydrogen or hydroxy.
- 03 7. The compound according to Claim 6, wherein R_1 is
04 hydrogen.
05
- 06 8. The compound according to Claim 1, wherein one of R_2
07 and R_3 is hydrogen or lower alkyl of 1 to 4 carbon
08 atoms, and the other is hydrogen.
09
- 10 9. The compound according to Claim 8, wherein one of R_2
11 and R_3 is hydrogen, methyl or ethyl, and the other is
12 hydrogen.
- 13 10. The compound according to Claim 9, wherein R_2 is
14 hydrogen, methyl or ethyl, and R_3 is hydrogen.
15
- 16 11. The compound according to Claim 1, wherein R_4 is a
17 polyalkyl group having an average molecular weight in
18 the range of about 500 to 3,000.
19
- 20 12. The compound according to Claim 11, wherein R_4 is a
21 polyalkyl group having an average molecular weight in
22 the range of about 700 to 3,000.
- 23 13. The compound according to Claim 12, wherein R_4 is a
24 polyalkyl group having an average molecular weight in
25 the range of about 900 to 2,500.
26
- 27 14. The compound according to Claim 1, wherein R_4 is a
28 polyalkyl group derived from polypropylene, polybutene,
29 or a polyalphaolefin oligomer of 1-octene or 1-decene.
30
- 31 15. The compound according to Claim 14, wherein R_4 is a
32 polyalkyl group derived from polyisobutene.
33
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- 01 16. The compound according to Claim 15, wherein the
 02 polyisobutene contains at least about 20% of a
 03 methylvinylidene isomer.
- 04 17. The compound according to Claim 1, wherein R is amino,
 05 R₁, R₂ and R₃ are hydrogen and R₄ is a polyalkyl group
 06 derived from polyisobutene.
 07
- 08 18. A fuel composition comprising a major amount of
 09 hydrocarbons boiling in the gasoline or diesel range
 10 and an effective deposit-controlling amount of a
 11 compound of the formula:
 12



18 or a fuel soluble salt thereof, wherein R is hydroxy,
 19 nitro or $-(CH_2)_x-NR_5R_6$, wherein R₅ and R₆ are
 20 independently hydrogen or lower alkyl having 1 to 6
 21 carbon atoms and x is 0 or 1;
 22

23 R₁ is hydrogen, hydroxy, nitro or $-NR_7R_8$, wherein R₇
 24 and R₈ are independently hydrogen or lower alkyl having
 25 1 to 6 carbon atoms;
 26

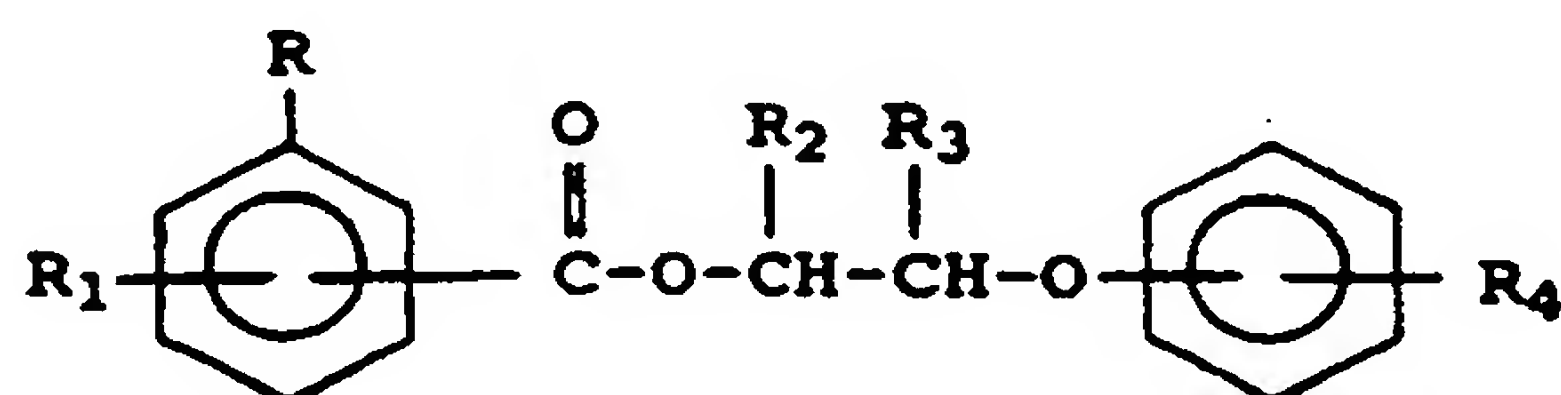
27 R₂ and R₃ are independently hydrogen or lower alkyl
 28 having 1 to 6 carbon atoms; and
 29

30 R₄ is a polyalkyl group having an average molecular
 31 weight in the range of about 450 to 5,000.
 32

- 33 19. The fuel composition according to Claim 18, wherein R
 34 is nitro, amino or $-CH_2NH_2$.

- 01 20. The fuel composition according to Claim 19, wherein R
02 is amino, or $-\text{CH}_2\text{NH}_2$.
- 03 21. The fuel composition according to Claim 20, wherein R
04 is amino.
05
- 06 22. The fuel composition according to Claim 18, wherein R_1
07 is hydrogen, hydroxy, nitro or amino.
08
- 09 23. The fuel composition according to Claim 22, wherein R_1
10 is hydrogen or hydroxy.
- 11 24. The fuel composition according to Claim 23, wherein R_1
12 is hydrogen.
13
- 14 25. The fuel composition according to Claim 18, wherein one
15 of R_2 and R_3 is hydrogen or lower alkyl of 1 to 4
16 carbon atoms, and the other is hydrogen.
17
- 18 26. The fuel composition according to Claim 25, wherein one
19 of R_2 and R_3 is hydrogen, methyl or ethyl, and the
20 other is hydrogen.
- 21 27. The fuel composition according to Claim 26, wherein R_2
22 is hydrogen, methyl or ethyl, and R_3 is hydrogen.
23
- 24 28. The fuel composition according to Claim 18, wherein R_4
25 is a polyalkyl group having an average molecular weight
26 in the range of about 500 to 3,000.
27
- 28 29. The fuel composition according to Claim 28, wherein R_4
29 is a polyalkyl group having an average molecular weight
30 in the range of about 700 to 3,000.
- 31 30. The fuel composition according to Claim 29, wherein R_4
32 is a polyalkyl group having an average molecular weight
33 in the range of about 900 to 2,500.
34

- 01 31. The fuel composition according to Claim 18, wherein R_4
 02 is a polyalkyl group derived from polypropylene,
 03 polybutene, or a polyalphaolefin oligomer of 1-octene
 04 or 1-decene.
- 05 32. The fuel composition according to Claim 31, wherein R_4
 06 is a polyalkyl group derived from polyisobutene.
 07
- 08 33. The fuel composition according to Claim 32, wherein the
 09 polyisobutene contains at least about 20% of a
 10 methylvinylidene isomer.
 11
- 12 34. The fuel composition according to Claim 18, wherein R
 13 is amino, R_1 , R_2 and R_3 are hydrogen and R_4 is a
 14 polyalkyl group derived from polyisobutene.
- 15 35. The fuel composition according to Claim 18, wherein the
 16 composition contains from about 50 to about 2,000 parts
 17 per million by weight of said compound.
 18
- 19 36. The fuel composition according to Claim 18, where the
 20 composition further contains from about 100 to about
 21 5,000 parts per million by weight of a fuel-soluble,
 22 nonvolatile carrier fluid.
 23
- 24 37. A fuel concentrate comprising an inert stable
 25 oleophilic organic solvent boiling in the range of from
 26 about 150°F. to 400°F. and from about 10 to about 70
 27 weight percent of a compound of the formula:



32
 33 or a fuel soluble salt thereof, wherein R is hydroxy,
 34 nitro or $-(\text{CH}_2)_x-\text{NR}_5\text{R}_6$, wherein R_5 and R_6 are

- 01 independently hydrogen or lower alkyl having 1 to 6
02 carbon atoms and x is 0 or 1;
03
04 R_1 is hydrogen, hydroxy, nitro or $-NR_7R_8$, wherein R_7
05 and R_8 are independently hydrogen or lower alkyl having
06 1 to 6 carbon atoms;
07
08 R_2 and R_3 are independently hydrogen or lower alkyl
09 having 1 to 6 carbon atoms; and
10
11 R_4 is a polyalkyl group having an average molecular
12 weight in the range of about 450 to 5,000.
13
14 38. The fuel concentrate according to Claim 37, wherein R
15 is nitro, amino or $-CH_2NH_2$.
16
17 39. The fuel concentrate according to Claim 38, wherein R
18 is amino, or $-CH_2NH_2$.
19
20 40. The fuel concentrate according to Claim 39, wherein R
21 is amino.
22
23 41. The fuel concentrate according to Claim 37, wherein R_1
24 is hydrogen, hydroxy, nitro or amino.
25
26 42. The fuel concentrate according to Claim 41, wherein R_1
27 is hydrogen or hydroxy.
28
29 43. The fuel concentrate according to Claim 42, wherein R_1
30 is hydrogen.
31
32 44. The fuel concentrate according to Claim 37, wherein one
33 of R_2 and R_3 is hydrogen or lower alkyl of 1 to 4
34 carbon atoms, and the other is hydrogen.

- 01 45. The fuel concentrate according to Claim 44, wherein one
02 of R₂ and R₃ is hydrogen, methyl or ethyl, and the
03 other is hydrogen.
04
- 05 46. The fuel concentrate according to Claim 45, wherein R₂
06 is hydrogen, methyl or ethyl, and R₃ is hydrogen.
07
- 08 47. The fuel concentrate according to Claim 37, wherein R₄
09 is a polyalkyl group having an average molecular weight
10 in the range of about 500 to 3,000.
11
- 12 48. The fuel concentrate according to Claim 47, wherein R₄
13 is a polyalkyl group having an average molecular weight
14 in the range of about 700 to 3,000.
15
- 16 49. The fuel concentrate according to Claim 48, wherein R₄
17 is a polyalkyl group having an average molecular weight
18 in the range of about 900 to 2,500.
19
- 20 50. The fuel concentrate according to Claim 37, wherein R₄
21 is a polyalkyl group derived from polypropylene,
22 polybutene, or a polyalphaolefin oligomer of 1-octene
23 or 1-decene.
24
- 25 51. The fuel concentrate according to Claim 50, wherein R₄
26 is a polyalkyl group derived from polyisobutene.
27
- 28 52. The fuel concentrate according to Claim 51, wherein the
29 polyisobutene contains at least about 20% of a
30 methylvinylidene isomer.
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- 01 53. The fuel concentrate according to Claim 37, wherein R
02 is amino, R_1 , R_2 and R_3 are hydrogen and R_4 is a
03 polyalkyl group derived from polyisobutene.
04
- 05 54. The fuel concentrate according to Claim 37, wherein the
06 fuel concentrate further contains from about 20 to
07 about 60 weight percent of a fuel-soluble, nonvolatile
08 carrier fluid.
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/07990

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C10L 1/18, 1/22

US CL : 044/399, 400 560/019, 020, 037, 061, 103

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 044/399, 400 560/019, 020, 037, 061, 103

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3,005,828 A (BALDRIDGE) 24 October 1961 (24-10-61) column 2, lines 25-66.	1-17
A	US 5,103,039 A (REARDAN et al) 07 April 1992 (07-04-92) column 2, lines 29-48.	1-17
A	US 4,515,981 A (OTANI et al) 07 May 1985 (07-05-85)	1-17
A	US 5,366,519 A (CHERPECK) 22 November 1994 (22-11-94)	1-54
A	US 5,380,345 A (CHERPECK) 10 January 1995 (10-01-95) column 4, lines 12-65.	1-54
A	US 5,427,591 A (CHERPECK) 27 June 1995 (27-06-95) column 4 lines 17-60.	1-54

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* *A* *E* *L* *O* *P*	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance earlier document published on or after the international filing date document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed	*T* *X* *Y* *A*	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art document member of the same patent family
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Date of the actual completion of the international search

12 JUNE 1997

Date of mailing of the international search report

03 SEP 1997

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